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THE ^{13}C NMR CONFORMATIONAL ANALYSIS OF 9,10-DIHYDROANTHRACENE MONOANIONS

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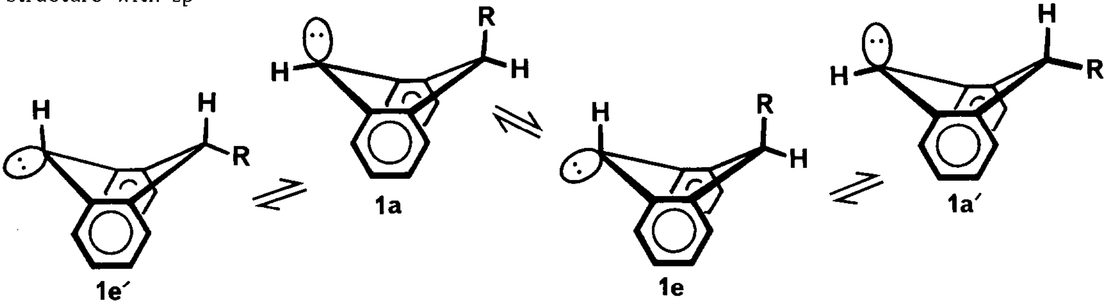
Summary: The ^{13}C NMR chemical shifts and coupling constants for the parent and t-butyl 9,10-dihydroanthraceneyl lithiums indicate sp^2 hybridization and flattened geometries.

The 9,10-dihydroanthracene monoanion (1, R = H) has generally been regarded as an inverting boat structure with sp^3 hybridization at the anionic center[1] despite an earlier proton NMR study[2,3] suggesting sp^2. This resulted primarily from the stereochemical outcome of a number of alkylation studies which seemed best rationalized by this model.[1] For example, the reaction of 1 (R = H) with alkyl halides leads to cis products when R'X is small, but trans products as R and R'X are increased in size. Since large R groups are known to strongly prefer the pseudoaxial position, 1a has been considered as the predominant species, but alkylation of 1e could be faster for large R'X (due to steric effects in 1a), even though it may be in low concentration. A suggestion that these anions are planar,[4] and that the stereochemistry results from the alkylation of different types of ion pairs has not met with much acceptance.[1k,m]

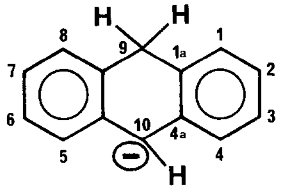


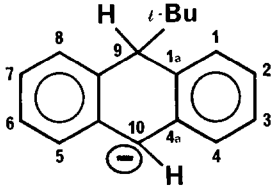
Structures such as 1e and 1e' would allow little overlap between the aromatic rings and the anionic center, and the possibility of a "flattened boat" with sp^2 hybridization has been considered.[5] In view of the recent proton NMR study by Bouas-Laurent, et.al.,[3] together with molecular mechanics calculations[6] suggesting planar or nearly planar structures for 9,10-dihydroanthracenes (DHA), further, direct spectroscopic studies appear warranted. Carbon-13 NMR is a useful tool for the determination of electron delocalization and conformational preference in charged species.[7]

DHA-Li and 9-*t*-BuDHA-Li were generated by proton abstraction with n-butyllithium in THF followed by evaporation to dryness and addition (condensation) of anhydrous ammonia.[8] Ammonia was chosen since it is a powerful solvent for anions, and problems with aggregation and covalent carbon-metal bonding can be avoided. In addition, our interest in anions as intermediates in metal-ammonia reduction makes spectroscopic studies in this solvent desirable for comparison with reaction conditions. Chemical shifts and one bond ^{13}C-H coupling constants at the anionic center are provided in Table 1.

One bond C-H coupling at the α carbon can provide useful information about hybridization, but ambiguities arise since these values are affected by the negative charge.[7a,9] However, this effect leads to a decrease in the coupling constant and so the values for DHA-Li (J = 151.6 Hz) and *t*-BuDHA-Li (J = 148.9 Hz) easily fall within the range for sp^2 hybridization.

Chemical shift assignments for the aromatic carbons were made as follows. For arylmethyl anions, the para carbons are known to experience the greatest upfield shift[7a,10] and were so





assigned (i.e., C_2/C_7). After the para positions, the ortho carbons experience the next strongest upfield shift,[10] and C_4 and C_{1a} could be assigned. Moreover, C_4 and C_{1a} could be distinguished by the coupled spectrum. The distinction between C_1 and C_3 in DHA-Li is not important since they are separated by only 0.025 ppm. In *t*-BuDHA-Li, C_1 and C_3 were assigned on the basis that these meta carbons would have nearly the same chemical shift as the neutral precursor. The chemical shifts for DHA have previously been reported. For *t*-BuDHA, the coupled spectrum produced the characteristic pattern referred to as the "fingerprint method" for α and β carbons of ortho disubstituted benzenes.[11] Hence we knew that C_1 and C_4 were 131.2 and 128.6 ppm, but did not know which was which. However, since C_1 is meta in the anion we knew it would be slightly (0.5-2 ppm) downfield in the neutral,[10] and C_1 was assigned as 131.2 based on the observation of a 130.5 signal in the anion. C_{4a} and C_{8a} cannot be distinguished, but this is unimportant since they differ by only 0.5 ppm. C_{4a} was easily assigned due to the expected downfield shift. C_{10} was assigned in DHA-Li from the coupled spectrum, and in *t*-BuDHA-Li by similarity in chemical shift to DHA-Li.

The ^{13}C assignments show significant upfield shifts, characteristic of substantial delocalization.[10] This again suggests sp^2 hybridization as well as a high degree of coplanarity. The ortho and para carbons are most sensitive to charge, and Olah[10f] has suggested that the para position is the best indicator of delocalization since it is less sensitive to substituent effects. Data for several systems are presented in Table 2, and we note that little difference is observed between Li$^+$ and K$^+$ salts when at least two aromatic rings are in conjugation. Hence we are justified in considering lithium salts with the DHA system. Grutzner[10e] has demonstrated by DNMR that the potassium salt of 7-phenylnorbornane is copolanar and the lithium salt pyramidal. This provides a value of 35.2 ppm upfield shift for the para carbon of a coplanar system, and when statistically corrected for the total number of para carbons (see Table 2), other benzyl anions considered as coplanar also provide similar values.

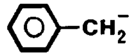
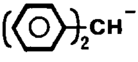
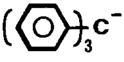
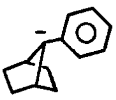
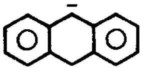
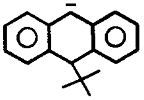
We can conclude that the DHA anions studied herein vibrate near or around a planar geometry with sp^2 hybridization at C_α. It is particularly interesting to note that the large *t*-butyl substituent seems to have little effect on the geometry of the anion as evidenced by ^{13}C NMR data. However,

Table 1. 75.46 MHz ^{13}C NMR Results for 9,10-Dihydroanthracene, t-Bu-9,10-Dihydroanthracene and their Lithium Salts.[a,b,c]

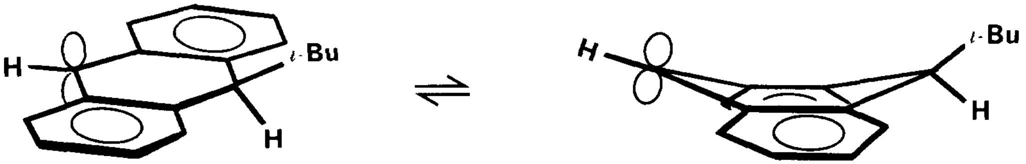
	C_1(m)	C_2(p)	C_3(m)	C_4(o)	C_{4a}(i)	C_{1a}(o)	C_{10}(α)	$J_{C10-H10}$(Hz)
DHA	127.8	126.5	126.5	127.8	137.5	137.5	36.6	123.9
DHA-Li[e]	126.0[d]	108.8	126.0[d]	114.0	145.6	119.8	78.7	151.6
t-BuDHA	131.2	126.6	125.6	128.6	138.7	138.2	37.6	124.0
t-BuDHA-Li[f]	130.5	107.5	125.3	115.5	144.7	118.6	81.3	148.9

a. In NH_3/THF at -50°C. b. Anion samples sealed in an 8 mm tube coaxially mounted in a 12 mm tube containing 50/50 CCl_4 acetone-d_6 for internal lock and temperature measurement (J. L. Led and S. B. Peterson, J. Magn. Reson., 1978, 32, 1). c. The THF signal measured at 68.05 ppm with internal TMS in the neutrals was used as reference in the anions. d. C_1 and C_3 are actually separated by 0.025 ppm. e. C_9 at 39.6 ppm. f. C_9 at 58.8 ppm, t-butyl (q) at 40.6, t-butyl (CH_3) at 28.0.

Table 2. ^{13}C NMR Chemical Shift Increments at Ortho and Para Positions for Arylmethyl Carbanions.[a]

Anion	$\Delta\delta C_o$		$\Delta\delta C_p$		$\Delta\delta C_p$ (Statistical Correction)	Reference
	K^+	Li^+	K^+	Li^+		
	18.0	12.0	30.5	21.6	30.5[d]	10d
	12.2	11.4	18.7	19.1	37.4[d]	10d
	5.6	4.8	13.1	13.7	39.2[d]	10d
	20.7	10.5	35.2	19.0	35.2[d]	10e
	—	15.8[f]	—	17.7	35.4	
	—	16.4[f]	—	19.1	38.2	

a. Difference in ^{13}C chemical shifts (ppm) between carbanions and corresponding neutral compound. b. In THF. c. In NH_3/THF. d. Potassium salts. f. Average of both ortho positions.



overlap has a cos θ dependence and small geometry changes will not produce substantial effects. We suggest that t-BuDHA-Li "vibrates"[12] between a planar state and a geometry involving a shallow boat with substituent pseudoaxial. Presumably a smaller substituent would result in a decreased amplitude of this vibration.

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12. As distinguished from an inversion process involving passage through a maximum (transition state).

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